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FINAL REPORT - PART I

HYDROGEN TRACER STUDIES ON THE REACTIONS OF URANIUM

HYDRIDE WITH AQUEOUS OXIDIZING AGENTS

by

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Hydrogen Tracer Studies on the Reaction of Uranium Hydride
with Aqueous Oxidizing Agents

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Summary

The reaction of UD_3 with concentrated HCl in H_2O forms HD as the principal gaseous product. When the concentration of the acid is reduced to ca. 9.5 $\underline{M}$, reaction is much slower, and H_2 and D_2 are the chief gaseous products. Little D is lost to the solvent by exchange, although this does become a feature of the results at still lower acidity. The rates of the reaction are very sensitive to the anion which is present. When Ce(IV) for example is the oxidizing agent, the D_2 originally contained in the solid is liberated essentially quantitatively and no other gaseous product is formed. These and related results are interpreted on the assumption that a barrier layer, presumably UO_2, governs the rate and mechanism of the reaction.

The main reactions of the salt-like hydrides NaH and LiH[1] with D_2O can be expressed by equations of the type:

$$MH + D_2O = HD + M^+ + OH^-.$$

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(1) H. Beutler, G. Brauer and H. O. Junger, Naturwiss., **24**, 347 (1936).

Also in the reaction of the complex hydride $LiAlH_4$[2] with D_2O, HD is the dominant gaseous product.[3] Preliminary experiments[4] with the metal-like

(2) I. Wender, R. A. Friedel and M. Orchin, J. Am. Chem. Soc., 71, 1140 (1948).

(3) The reaction of $LiAlH_4$ with D_2O has been recommended as a way to prepare pure HD. However, when KBH_4 is the reactant, there is a substantial admixture of H_2 and D_2 in the gases. W. L. Jolly and R. E. Mesmer, J. Am. Chem. Soc., 83, 4470 (1961).

(4) U. Agarwala, J. B. Hunt and H. Taube, J. Chem. Phys., 32, 1567 (1960).

hydride UH_3 showed that the mechanism of dissolution for it can be quite different from that implied by equation 1. In 11 $\underline{M}$ DCl, the reaction of UH_3 is slow and yields a gas in which H_2 and D_2 rather than HD are the dominant species, and the principal reaction taking place under these conditions is described by the equation

$$UH_3 + 4D^+ = U^{+4} + 3/2\,H_2 + 2D_2$$
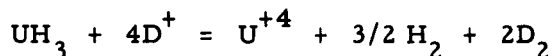
In very concentrated DCl the reaction is rapid, even violent and under these conditions HD becomes the principal gaseous product.

In this paper, a more detailed investigation of the isotopic course of the reactions of uranium hydride with acids is described, and the study has been extended to include other oxidizing agents as well. For them, even the stoichiometry is a matter of considerable interest because all of the reagents used have the capacity to oxidize hydrogen; thus it is of interest to learn to what extent hydrogen is evolved by their action. Preliminary results for CeH_3 and TiH_2 which are of interest for comparison purposes are also described.

Experimental

Reagents and preparations. --Uranium metal used in the preparation

of the hydrides or deuteride was first treated with 8 N HNO_3 to remove the

oxide coating, then washed with distilled water and dried in vacuo. UH_3 was

prepared from massive metal in an apparatus like that described by Spedding

et al.[5] The hydrogen tracer experiments are more economically done using

(5) F. H. Spedding, A. S. Newton, J. C. Warf, O. Johnson, R. W. Nottorf, I. B. Johns and D. Daane, Nucleonics, 4, No. 1, 4 (1949).

UD_3 in a solvent of normal isotopic composition, and all of the experiments

after the preliminary ones were done in this way. The uranium was of the

highest purity and was used in the form of foil. D_2 was purified by passing

it through a liquid air trap and then absorbing it in uranium metal. It was

released from the metal by heating the solid to 650° while the weighed sample

to be converted to the deuteride was maintained at 250°. The deuterium used

for reaction was contained in a closed volume, and for the later preparations,

the amount of D_2 consumed was measured by a gas burette so that the compo-

sition of the deuteride could be calculated. The UH_3 or UD_3 prepared by us

was undoubtedly in the beta-modification.[6]

(6) B. M. Abraham and H. E. Flotow, J. Am. Chem. Soc., 77, 1446 (1955).

Titanium and zirconium hydrides were obtained from Metal Hydrides,

Inc. The sample of cerium hydride was prepared by heating Ce (99.5% pure)

in a stream of dry hydrogen for 4 hours.

DCl was produced by adding PCl_3 to excess D_2O in a closed system. The gas was absorbed in D_2O at 0°C to produce DCl solutions. D_2SO_4 and D_3PO_4 solutions were prepared by mixing the corresponding anhydrides with D_2O.

$Ce(HSO_4)_4$ was converted to $Ce(DSO_4)_4$ by successive additions of D_2O in small amount followed by heating to dryness. $TlCl_3$ in D_2O was prepared by oxidizing a suspension of anhydrous TlCl with Cl_2, then removing the excess Cl_2 with a stream of dry N_2. Anhydrous $FeCl_3$ was prepared by the reaction of Cl_2 with Fe wire.

O_2 enriched in O^{18} was prepared by thermal decomposition of HgO. The O^{18} enriched HgO was obtained by the reaction of $HgCl_2$ with O^{18} enriched alkali.

Isotopic analyses. --Analyses for the H_2-HD-D_2 content of the gases were made with a Consolidated 21-620A Analytical Mass Spectrometer. A correction for the change in sample pressure during analysis was made by extrapolation to zero time, and for the contribution of H_3^+ to the HD^+ peaks by extrapolation to zero pressure.[7] Isotopic ratios thus determined were

(7) I. Friedman, Geochimica et Cosmochimica Acta, 4, 89 (1953).

precise to 1%. The validity of the measurements of isotopic composition was tested by mixing measured volumes of H_2 and D_2. A mixture calculated to contain 40.4 mole per cent H_2 analyzed as 40.5 mole per cent. To determine whether dilution by H occurred during the preparation and handling of the D-rich solution, samples of hydrogen were prepared by the reaction of the acid

solutions with Mg. No appreciable dilution of D_2O was found to have taken place.

The analysis for the O^{18} content of the residue left by the reaction of acid with the hydride was done by the Anbar-Guttmann[8] method.

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(8) M. Anbar and S. Guttmann, J. Appl. Rad. Isotopes, 5, 233 (1959).

<u>Chemical analyses.</u> --H_2 was measured manometrically, as was O_2. When O_2 was admixed with H_2, the amount was determined by noting the decrease in pressure attendant on absorbing O_2 in alkaline pyrogallol or in acidic $Cr^{++}aq$.

The U content of the solutions resulting from the dissolution of the hydride in ceric sulfate solution was determined by reducing U to the tetrapositive state with a Jones reduction, then titrating U(IV) with Ce(IV).[9]

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(9) I. M. Kolthoff and B. Belcher, "Volumetric Analysis," Vol. III, Interscience Publishers, New York, N. Y., 1957.

Uranium hydride was analyzed by adding a weighed sample to an excess of ceric sulfate solution. The H_2 evolved, the Ce(IV) consumed and the U contained in the solutions were determined. Uranium hydride is consumed completely and the stoichiometry of the reaction of the hydride with Ce(IV) conforms closely to the equation:

$$UH_3 + 6Ce^{+4} + 2H_2O = UO_2^{++} + 6Ce^{+3} + 4H^+ + 3/2\,H_2.$$
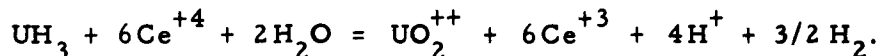
As evidence in support of this conclusion, the data of Table I are offered.

Table I

Dissolution of Uranium Hydride in Ceric Sulfate Solution

(Ce(IV), 0.219 $\underline{M}$; H_2SO_4, 1.0 $\underline{M}$)

|	
H/U for hydride	2.94
Ce(IV) consumed, equiv./g. atom U	6.05
H_2 evolved, mole/g. atom of U	1.48

Procedure. --In the early stages of the research, the UH_3 which was prepared was stored in a sealed ampoule, and samples as needed were weighed and transferred in the N_2 atmosphere of a dry-box. The hydride is very re-active, and in spite of precautions taken in the transfer, different samples showed variations in composition, presumably owing to reaction during trans-fer. In view of this difficulty, the hydride for the later experiments was pre-pared separately for each run in a side arm of the vessel in which the dissolu-tion reaction was carried out. To initiate reaction the reagent solution was admitted, under atmospheric pressure, into the evacuated vessel containing the hydride. A teflon-coated stirring bar was included in the reaction vessel. The vessel was fitted with a ground glass joint to facilitate connection to a vacuum train or the pressure measuring device. Reactions were carried out at ambient temperature.

Results

It is necessary for the presentation and discussion of the results to distinguish between hydrogen, as comprised by all species of atomic number one, and the different isotopic forms of the elements. When no differentiation

with respect to mass is called for, the terms "hydrogen" or "hydride" will be used, and formulas will be used to identify the isotopic species.

When hydrogen ion is the only oxidizing agent, U(IV) is expected as the product in the oxidation, and the reaction is expected to conform to the stoichiometry expressed by the equation

$$UH_3 + 4H^+ = U^{+4} + 7/2\,H_2. \tag{1}$$
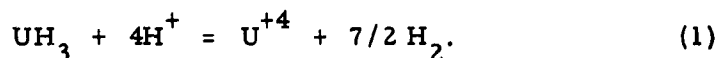
The deviations from this equation have two causes: (a) not all the hydride is dissolved; (b) the hydridation of the uranium is incomplete. For the experiments in which the composition of the hydride is unknown, for want of a better basis, the per cent of theoretical hydrogen evolution is calculated with reference to equation 7. In the experiments for which the composition of the hydride was determined (as UH_n for example), 100% evolution of hydrogen is taken as conforming to the equation

$$UH_n + 4H^+ = U^{+4} + \frac{4+n}{2}\,H_2 \tag{2}$$
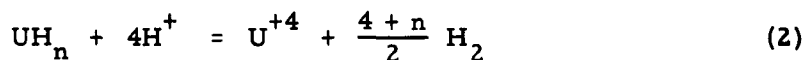
The experiments with oxidizing agents such as Ce^{+4}, Ag^+ etc. are discussed with reference to the equation

$$2H_2O + UH_n = n/2\,H_2 + UO_2^{++} + 4H^+ + 6e^- \tag{3}$$
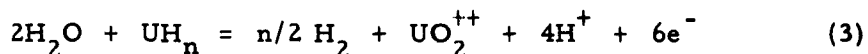
as representing the theoretical stoichiometry for the hydride half-reaction.

The time of reaction recorded in the tables is the total time elapsed from the time of mixing. At the time recorded all the gas was removed so that the succeeding sample, if any, represents the gas liberated in the next time interval.

A. **The Dissolution of Uranium Hydride in Aqueous Acids**

1. **Hydrochloric Acid.** --In Table II we record some experimental re-sults which serve to confirm the general nature of the results which were reported earlier. The reaction in 16 $\underline{M}$ DCl is rapid and HD is the predominant form of the gas evolved. At lower acid (cf. exp. 8), the reaction becomes much slower, and H_2 and D_2 are the dominant forms in the gas phase.

Table II

The Isotopic Course of the Reaction of UH_3 in
Strong DCl Solution

Exp. No.	Time of Reaction, hr.	Ave. (DCl)	H_2/HD	D_2/HD	D/H
3		16	0.11	0.19	1.13
4	1.7×10^2	16	0.18	0.40	1.32
2	8.9×10^2	14.5	1.02	1.40	1.25
8	5.2×10^2	9.0	4.9	14.5	--

The reaction of the hydride with hydrochloric acid solution is in no case complete, even when, as for experiments 3 and 4, the reaction is violent in the initial stages.

The results of a number of experiments using hydrochloric acid at 10 $\underline{M}$ or lower in concentration are summarized in Table III.

An attempt was made in two of the experiments at chemical analysis of the black residue. The analysis was done by adding the residue to ceric sulfate solution, determining the consumption of Ce(IV) in this step, and

Table III

Stoichiometry and Isotopic Course of the Reaction of UD_3 in Aqueous HCl

Exp. No.	H/U	(HCl), Ave.[a]	Sample No.[b]	Time, hr.[b]	Hydrogen Evolved % Theory[c]	H_2/HD	D_2/HD	H/D
9	--	9.8	1	4.6×10^3	85	12.0	8.8	1.35
10	--	9.8	1	0.25	10	17.8	9.1	1.91
			2	0.50	5.7	16.2	11.8	1.36
			3	20	40.5	11.8	7.0	1.64
			4	44	0.7	7.0	5.0	1.36
19	2.91	9.5	1	288	83.4	11.2	7.8	1.41
12	--	9.4	1	5	71.3	15.1	11.0	1.36
			2	25	11.3	11.5	7.2	1.56
			3	49	0.2	6.5	2.9	2.1
13	2.96	9.5	1	0.05	4.3	6.9	3.6	1.80
			2	48	90.7	9.6	6.6	1.42
15	2.94	4.7	1	192	15.4	3.72	2.02	1.67
			2	1.2×10^3	46.5	5.49	2.28	2.16
16[d]	--	4.7	1	68	88.2	9.88	7.10	1.37
17[e]	2.62	2.2	1	0.17	17.5	19.2	7.7	2.4
			2	14	30.4	18.1	7.7	2.4
			3	168	43.7	11.7	4.2	2.5

[a]The change during an experiment in no case exceeded 4%

[b]The time in each case represents that elapsed from the time of mixing.

[c]100% theory corresponds to equation 1 (or 2 when initial D/U is known).

[d]5.2 M LiCl.   [e]7.6 M LiCl.

then determining the U content of the solution. In calculating the average oxidation state of the uranium, it was assumed that hydride-hydrogen was liberated with no loss by ceric oxidation (cf. Table I). The average oxidation state of uranium in the residue from one of the experiments was calculated as 2.36 and as 2.20 for the other. The total hydrogen evolved was not measured; its isotopic composition was found to correspond to 98.2% H_2, even though the reaction medium was completely deuterated. The chloride content of the residues was found to correspond to less than 1 chloride for each 35 uranium atoms.

The residue from experiment 18 was collected, washed in N_2-saturated dilute HCl, transferred to a glass plate and dried in vacuo. After drying, it was placed in the beam of an X-ray diffractometer. In Table IV, the peaks observed between 25° and 77° for 2 Θ are shown and are compared with those reported for UO_2.

Table IV

Powder Diffraction Pattern for Residue
(Cu Kα Source; 25° < 2Θ< 77°)

Observed	28.3	32.7	47.0	55.7	58.5	68.6	75.9
Reported[10]	28.26	32.74	46.97	55.75	58.4	68.59	78.30

(10) H. J. Garrett and R. E. Brocklehurst, Wright Air Development Center Technical Report 57-381, p. 10 (1958).

Sulfuric acid. --UH$_3$ was found to react vigorously in 9.4 $\underline{M}$ H$_2$SO$_4$ and the hydride was completely consumed in 16 hr. at room temperature. Some reduction at least of SO$_4^=$ took place, as evidenced by the odor of H$_2$S which became apparent when the reaction vessel was opened. The isotopic composition (H$_2$:HD:D$_2$) of the hydrogen formed was found to be 0.81:1.00:3.23.

A sample of UD$_3$ prepared in situ was brought into contact with 2.0 $\underline{M}$ H$_2$SO$_4$. The reaction began vigorously, but it virtually ceased within a few minutes, and after 16 hr. only 0.80% of the total hydrogen expected was evolved (H$_2$:HD:D$_2$ = 2.96:1.00:1.88).

Phosphoric acid. --The reaction of UH$_3$ with 85% D$_3$PO$_4$ began vigorously and appeared to be complete after 26 days. The hydrogen evolved constituted 89.2% of that expected assuming that the hydride was UH$_3$ (H$_2$:HD:D$_2$ = 0.63:1.00:2.4).

Hydrofluoric acid. --The reaction of UD$_3$ with 1.4 $\underline{M}$ HF is vigorous, and the bulk of the UH$_3$ was found to be consumed in a few minutes. The reaction was allowed to proceed for 14 hr., and although a copious precipitate, presumably UF$_4$, was present, it appeared to contain no black residue. The ratio H$_2$:HD:D$_2$ was measured as 1.73:1.00:1.25 giving H/D = 1.27. The results at 4 $\underline{M}$ HF were not substantially different and in this experiment H$_2$:HD:D$_2$ = 1.60:1.00:0.97 with H/D = 1.43.

B. The Reaction of Uranium Hydride in Solutions of Various Oxidizing Agents

A differentiation of the results obtained when hydrogen ion is the only oxidizing agents, and those obtained when other oxidizing agents are present

seems appropriate for two reasons. All of the oxidizing agents which were used except hydrogen ion are capable of oxidizing hydrogen and it is a matter of interest to learn whether hydrogen can be liberated when the hydride reacts in such solutions; in addition, the majority of the oxidizing agents (UO_2^{++} and hydrogen ion are the only exceptions) under the conditions used have the capability of oxidizing uranium to the +6 state. In fact, striking differences in behavior are noted when on the one hand hydrogen ion is the only oxidizing agent, and when on the other, stronger oxidizing agents are used. The results obtained with a number of oxidizing agents are summarized in Table V.

No residue was left in the experiments using $FeCl_3$ or Ce(IV) as oxidizing agents, and the visual evidence suffices for the conclusion that the dissolution was complete in these experiments. The reaction with $FeCl_3$ in concentrated acid was very rapid and was substantially complete in 5 min. The reactions in alkaline H_2O_2 and with Ce(IV) in H_2SO_4 are also very rapid, and the long reaction time was chosen only to ensure that reaction was really complete and to gain some assurance that rapid equilibration of hydrogen with the product solution does not take place. With $TlCl_3$ as oxidizing agent, TlCl is formed, and we judge from the white color of the final solid that oxidation was complete also in this case. Likewise, we judge from the yellow color of the uranyl peroxide residue that oxidation with H_2O_2 was complete. When $Fe(CN)_6^=$ is the oxidizing agent, reaction is vigorous, and a brown sludge, presumably uranyl ferro- or ferri-cyanide is produced. In spite of the vigor displayed by the reaction in the early stages, the process was apparently not complete in the reaction mixture left for 12 hours; however, since recovery

Table V

Stoichiometry and Isotopic Course of the Reaction of Uranium
Hydride with Various Oxidizing Agents

Reactants	D or H/U	Time hrs.	Hydrogen,[a] % Theory	H_2/HD	D_2/HD
UH_3; 0.9 $\underline{M}$ $FeCl_3$ in D_2O	--	72	89	32..3	0.03
UD_3; 1.2 $\underline{M}$ $FeCl_3$, 15 $\underline{M}$ HCl in H_2O	2.96	20	118	3.45	4.64
UH_3; 1.5 $\underline{M}$ $TlCl_3$ in D_2O	--	16	84.2	31.1	0.13
UD_3; 1.0 $\underline{M}$ $Fe(CN)_6^\equiv$, 0.7 $\underline{M}$ HCl in H_2O	2.93	12	89.5	2.0	68.3
UD_3; 1.1 $\underline{M}$ $Fe(CN)_6^\equiv$, 1.0 $\underline{M}$ HCl in H_2O	2.42	95	93.9	2.0	49.0
UH_3; 1.0 $\underline{M}$ $AgNO_3$ in D_2O	--	0.5	97	40.6	0.04
UD_3; 1.0 $\underline{M}$ H_2O_2 1.1 N H_2SO_4	--	16	96.0	0.66	33.1
UD_3; 1.0 $\underline{M}$ H_2O_2	--	14	69.5	0.5	26.4
UD_3; 1.0 $\underline{M}$ H_2O_2, NH_4Cl-NH_3 at pH 8.9	2.94	12	94.1	0.24	105
UD_3; 0.22 $\underline{M}$ Ce(IV) 2 N H_2SO_4	--	15	--	0.39	29.9
UD_3; 0.22 $\underline{M}$ Ce(IV) 2 N H_2SO_4	2.94	16	101	0.78	54.7

[a]100% theory taken as conforming to equation 3.

of D was essentially complete for the mixture left to react for 95 hr., the reaction must have been complete in this case. The reaction of uranium hydride with $AgNO_3$aq. proceeds rapidly. Since recovery of H_2 was approximately 96% of that assumed for a hydride of composition UH_3, it is likely that the hydride was completely consumed in this case. U(VI) appeared to be the main product of each of the reactions summarized in Table VI.

Several experiments were done with O_2 present in the acidic solutions, but the observations will be described in some detail only for the experiment which was the most complete. UD_3 (but with the initial composition not defined) was used in a medium 4.8 $\underline{M}$ in HCl and with O_2 at 0.4 atm. pressure. After 5 days the hydrogen evolved corresponded to 74% of the theoretical as defined by equation 3 assuming n = 3; the ratio D_2:HD:H_2 in the gas was measured as 12.0:1.00:0.94. It is entirely likely that hydride was left in the copious black residue which remained, yet the average oxidation number of the U in solution exceeded 4, and was found to be 4.32. The black residue was separated, washed with HCl aq. and dried. Its oxygen isotopic composition was found to correspond closely to that of the medium which was of normal isotopic composition; the O_2 gas was 8.07-fold enriched in O^{18}.

UO_2SO_4 at 0.99 $\underline{M}$ in 1.4 N H_2SO_4 was also used as the oxidizing mixture acting on UD_3. In 40 hr., reaction was only 4.6% complete. D_2:HD:H_2 in the gas was measured as 4.70:1.00:2.00.

C. Other Hydrides

<u>Cerium hydride</u>. --The reaction of CeH_3 in 10 N D_2SO_4 was complete in 5 hr. Isotopic analysis of the gas showed the ratio H_2:HD:D_2 to be

0. 180:1. 00:0. 196 with D/H = 1. 02. In an experiment using NaOD in D_2O as the reaction mixture, successive samples of gas were taken. Although the amount of gas in each sample was not determined it is of interest to record that the ratio D/H for successive samples changed from 1. 19 to 4. 8 to 5. 1 for samples collected after 2 hours, after 4 hours more and after 16 hours more. When 1 $\underline{M}$ $AgNO_3$ in D_2O was used as oxidizing mixture reaction was again rapid--it was apparently complete in 15 min. --and in the gas evolved H_2:HD:D_2 = 7. 38:1. 00:0. 093.

Titanium hydride. --No hydrogen was detected after a period of one year for titanium hydride in contact with 2. 3 $\underline{M}$ $TlCl_3$. The solution in the vessel was colorless, and no white precipitate of TlCl was observed. Nor was hydrogen detected after three days when the hydride was added to 0. 27 $\underline{M}$ Ce(IV) in 2 $\dot{N}$ H_2SO_4. In Table VI data are presented for two experiments concerned with the reaction of the hydride (presumed to be TiH_2) with 15 $\underline{M}$ and 7. 5 $\underline{M}$ DCl. The reaction was initially slow in both cases, but became vigorous after a few minutes. It was complete by the time the last sample was taken for 15 $\underline{M}$ DCl but not for 7. 5 $\underline{M}$.

Zirconium hydride. --The evolution of hydrogen from zirconium hydride was slow even in 15 $\underline{M}$ HCl. Since the hydride had been exposed to air, this behavior probably resulted from the coating of ZrO_2 which was almost certainly laid down on the material. The gas collected after one week was barely sufficient for mass-spectrometric analysis. It showed the ratios D_2:HD:H_2 as 3. 1:1. 00:1. 08.

Table VI

Dissolution of TiH_2 in DCl Solutions

Sample	Time, hr.	D_2/HD	H_2/HD	D/H
		15 M DCl		
1	1	1.75	0.98	1.52
2	2	1.71	0.94	1.55
3	3	1.70	0.97	1.50
4	4	1.80	0.97	1.56
5	15	2.03	1.05	1.63
		7.5 M DCl		
1	1	1.52	0.39	2.3
2	2	1.68	0.39	2.5
3	3	1.82	0.37	2.7
4	4	2.07	0.33	3.1
5	20	2.15	0.32	3.2
6	21	2.25	0.31	3.4
7	24	2.40	0.30	3.6

Discussion

The experiments of Table II confirm the conclusion that when concentrated (16 M) hydrochloric acid is the oxidizing medium, the dominant form of hydrogen is made up with one atom derived from the medium and the other from the hydride. They also lead to the conclusion that the H of the UH_3 is largely transferred to the gas phase in the deuterated reaction medium so that little exchange of hydride with hydrogen of water takes place. This follows because for the reaction:

$$UH_3 + 3D^+ = U^{+3} + 3(H) + 3(D),$$
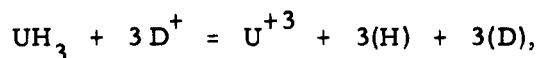
the expected ratio D/H when no exchange occurs is 1.00. In experiment 3, the value of D/H observed is only slightly in excess of this, and a small excess is to be expected because some U^{+4} was almost certainly formed. In experiments 2 and 4, the reaction of U^{+3} to U^{+4} was certainly complete, and for this experiment the ratio of D/H is close to the theoretical value of 1.33 expected for complete oxidation with no exchange. Since the dissolution of the solid was not complete in any case, slight deviations from ideal stoichiometry are ascribable to this cause, but the amount of unreacted material could not have exceeded 10% in experiment 2 or 4.

Experiments 9, 10, 12, 13 and 19 agree on the conclusion that when the reaction medium acting on UH_3 is ~9.5 $\underline{M}$ DCl, the principal forms of hydrogen become H_2 and D_2 rather than HD. In these experiments, too, the hydride-D is conserved: i.e. there is little exchange with the solvent. Thus, if it is assumed for experiment 19 that the hydride which has not reacted has the same composition as the starting material, the ratio of H/D computed for no D exchange is 4/2.91 = 1.38 compared to 1.41 observed. For experiment 13, in which consumption of UD_3 was most complete, theory and experiment compare as 1.36 and 1.44. For experiment 9, theory calls for H/D > 1.33 (where this is the value if the hydride has the theoretical composition $UD_{3.00}$) and the experimental value is 1.35.

The variations in the ratios H/D with extent of reaction show no uniform behavior, and the rates of reaction also are not closely reproducible.

At lower concentrations of HCl (see exp. 15 with HCl at 4.7 $\underline{M}$) the reaction rate becomes much less. HD becomes a much more important component of the gaseous mixture, and the H/D ratio shows that there is extensive exchange of D in UD_3 with the environment.

Anions exert a profound effect on the results when hydrogen ion is the oxidizing agent. Thus, comparison of experiment 16 (4.7 $\underline{M}$ HCl, 5.2 $\underline{M}$ LiCl) with 15 shows that LiCl restores the behavior of the system to that characteristic of 9.5 $\underline{M}$ HCl as the reaction medium. Even in relatively dilute HF, the reaction of uranium hydride is quite rapid. H_2, HD and D_2 are all present in approximately equal amounts. However, very little exchange of hydride-hydrogen with the solvent takes place. This particular result contrasts with the corresponding one obtained with 85% H_3PO_4 as the reaction medium.

Of the oxidizing agents that are capable of oxidizing U all the way to the +6 state, Ce(IV) exemplifies an ideal type of behavior: All the hydride hydrogen appears as gaseous product, and very little besides this. Deviations from this ideal behavior will be referred to in the discussion of the results.

The results obtained in this study can be understood by postulating a barrier layer; in fact the results at 9.5 $\underline{M}$ HCl which show that hydride-hydrogen and solvent hydrogen are kept effectively apart seem to be proof that a barrier layer exists under these conditions. Dissolution of the barrier layer and diffusion through it govern the behavior which we observed. Thus when very concentrated hydrochloric acid is the oxidizing agent, the barrier layer is thin, and perhaps non-existent for much of the reaction time so that reaction takes place largely by direct union of hydride with hydrogen ion.

At lower acid, say 9.5 $\underline{M}$ HCl, the barrier layer is thicker; its nature is such that e^- (or positive holes) and $O^=$ move more freely than do U cations or hydrogen ion. As a result, electrons flow outward (or positive holes inward) through the layer reducing the external oxidizing agent. The uranium being more oxidizable than the hydrogen in uranium hydride is converted to a cation at the barrier-hydride interface and there it reacts with incoming $O^=$. The hydrogen is not oxidizable in contact with hydride and is liberated in elementary form. When Ce(IV) rather than H^+ is the external oxidizing agent, the process is affected only to the extent that the reaction is more rapid because the barrier layer reacts with Ce(IV), and because Ce(IV) rather than H^+ absorbs the electrons that flow through the barrier layer from the solid hydride.

In view of the identification made of the residue from the reaction of hydrochloric acid with uranium hydride, it seems entirely reasonable to assume, as was done by Waber,[11] that the barrier layer is composed of UO_2.

(11) J. T. Waber, U. S. Atomic Energy Commission, TID-7587 (1959), pp. 307-387.

In every major respect, the oxide has properties needed for a barrier layer acting as described in the previous paragraph. The volume change when UH_3 changes to UO_2 is only about 11%, and thus the strain resulting from the transformation should not be large. UO_2 is a p type semiconductor,[12] requiring an activation of only 0.4 e.u. to free a positive carrier from an interstitial

(12) P. K. Willardson, J. W. Moody and H. C. Goering, J. Inorg. and Nuclear Chem., 6, 19 (1958).

position, thus it seems reasonable that electron conduction (by positive hole transfer) would be more facile than proton transport. Self-diffusion[13, 14] and marker[15] experiments have shown that oxide ion and not U^{+4} ion is the

(13) J. Belle and B. Lustman, U. S. Atomic Energy Commission, TID-7546, 1957, p. 442.

(14) A. B. Auskern and J. Belle, J. Chem. Phys., 28, 171 (1958).

(15) J. G. Schnizlein, J. D. Woods, J. D. Bingle and R. C. Vogel, J. Electrochem. Soc., 107, 783 (1960).

mobile species in UO_2. The thermodynamic properties of UO_2 are such that though it is stable with respect to $UH_3 + H_2O$, it is unstable with respect to U^{+4} and H_2O in strong acid. The latter conclusion follows from the values of ΔF° for $UO_2(s)^{16}$ and U^{+4} and H_2O^{17} which have been recorded. These

(16) E. G. Huber, C. E. Holley and E. H. Meyerhoff, J. Am. Chem. Soc., 74, 3406 (1952).

(17) W. M. Latimer, "Oxidation Potentials," Prentice-Hall, Inc., 2nd edition, pp. 302, 39.

give as equilibrium quotient for the reaction

$$UO_2 + 4H^+ = U^{+4} + 2H_2O$$
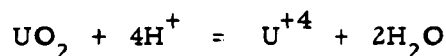
the value of 6×10^3. Thus UO_2 would not be expected as an equilibrium product in 1 $\underline{M}$ H^+. The rates of dissolution are slow, and the many vagaries of the system can be ascribed to the differing rates of dissolution of oxide under different conditions.

Thus, the influence that the anions exert on the rate and isotopic behavior when H^+ is the oxidizing agent may find an explanation in terms of differing rates of dissolution of oxide when different anions are present.

It seems possible that the affinity which U^{+4} has for Cl^- is exploited in bring-ing about more rapid dissolution of UO_2 when Cl^- is present. Similarly, F^- and $PO_4^{\equiv}$ may keep the oxide layer very thin or remove it altogether, in these cases exploiting the stabilities of the fluoride and phosphates of U^{+4}. The dramatic decline in rate which is observed as the reaction in dilute HCl pro-gresses finds the reasonable explanation that since no ready means of dissolv-ing the oxide is at hand, it continues to build up. The more rapid rates ob-served when oxidizing agents known to dissolve UO_2 are present are ascribable to the fact that the barrier layer will be thinner in these cases.

While it is necessary to invoke the dissolution of the barrier film as a factor in understanding the results, it seems necessary in addition to assume that attack by H_2O (to form UO_2) and by H^+ are competing processes. Reaction of the hydride with H_2O forms UO_2; when the oxide film is kept from develop-ing, direct reaction of protons from the solvent with hydride hydrogen becomes possible. The experiment with $FeCl_3$ in concentrated HCl shows that the direct action is not limited by hydrogen ion; for in this experiment, conducted with UD_3, the total amount of D recovered in the gas is considerably less than that brought in with UD_3, and it is entirely reasonable to assume that in this case the hydride-hydrogen is not protected from oxidation by the ferric chloride. The equation expressing the stoichiometry of the reaction of $UD_{2.96}$ with $FeCl_3$ in concentrated HCl is as follows:

$$5.46\,Fe(III) + UD_{2.96} + 0.54\,H^+ = 1.98\,[D] + 1.52\,[H] + U(VI) +$$
$$5.46\,[Fe(II)].$$
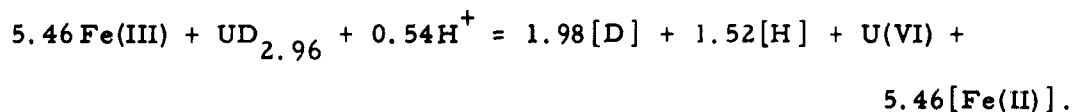
The conservation of the hydride-hydrogen in the other experiments with oxidizing agents at lower concentrations of acid thus argues for the presence of a barrier layer in each of these cases. The effect which is the most difficult to understand is the exchange of hydride-hydrogen with solvent-hydrogen which is observed under some conditions. The extent of this exchange was quite large in the experiment with 4.7 $\underline{M}$ HCl. It appeared also in the experiment with H_3PO_4 as oxidizing agent, to a small extent (probably) when $Fe(CN)_6^=$ is the oxidizing agent, and to a considerable extent in the experiment with O_2 as oxidizing agent. The experiments with concentrated HCl as the oxidizing agent show that direct contact of solvent-hydrogen with hydride-hydrogen by no means is sufficient to ensure the exchange. In these experiments, hydride-hydrogen was transferred almost quantitatively to the gas phase. It is possible that under some conditions the barrier layer is permeable to H and under these conditions the exchange takes place.

Two points in connection with the observations made with O_2 as oxidizing agent seem worthy of special mention. The oxygen in the oxide layer was found to have been derived from the solvent rather than the O_2. Although the result is consistent with the hypothesis we have advanced, it does not provide additional support. Exchange of massive UO_2 with solvent is known not to be rapid, but exchange at the surface as UO_2 develops slowly may be rapid enough to ensure the isotopic identity of the UO_2 and solvent oxygen. It appears fairly definite that the reaction of UO_2 in 4.8 $\underline{M}$ HCl with oxygen present is more rapid than when HCl alone is used. In the experiment, the average oxidation state of U in solution was found to be 4.3. The enhanced reaction

rate may result from the fact that the oxide layer contains oxygen in excess

of the stoichiometry UO_2. The oxygen self-diffusion coefficient in $UO_{2.064}$

has been shown to be 15.4 times as rapid as it is in $UO_{2.004}$.[18]

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(18) J. Belle and A. B. Auskern, "Kinetics of High Temperature Processes," John Wiley & Sons, Inc., New York, N. Y., 1959, pp. 44-49.


It is interesting to compare the reactions of MgH_2, UH_3 and palladium

hydride with Ce(IV) in solution. When MgH_2 is the reactant, Ce(IV) is not at

all involved in the net change.

$$MgH_2 + 2H^+ = Mg^{+2} + 2H_2.$$
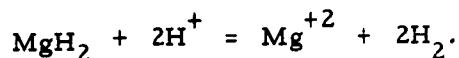
When UH_3 is used, the metal is oxidized, but not the contained hydrogen

$$UH_3 + 6Ce(IV) + 2H_2O = UO_2^{++} + 6Ce^{+3} + 3/2H_2 + 4H^+$$
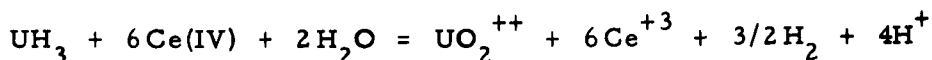
When PdH_2 reacts, the contained hydrogen, but not the metal, is oxidized.

$$PdH_n + nCe(IV) = Pd + nCe^{+++} + n/2 H_2.$$
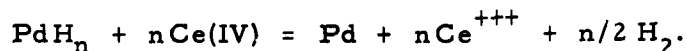
The results obtained with cerium hydride and titanium hydride though

meager, do lead to some definite conclusions. The experiment with D_2SO_4 as

oxidizing mixture shows that the sample of hydride used had nearly the theo-

retical formula CeH_3 and that the contained hydrogen is transferred almost

quantitatively to the gas phase. This follows because D/H was found to be

1.02 and thus X in the equation

$$Ce\ H_X + 3D^+ = Ce^{+3} + 3[D] + X[H]$$
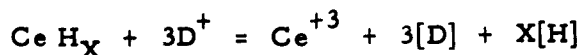
is at least 2.94. In alkaline solution, there is considerable loss of H to sol-

vent. Furthermore, the proportion of deuterium in the gas evolved was found

to increase with each succeeding sample, thus indicating exchange of the bulk

hydride with the solvent. Reasoning similar to that applied to the reaction of

D_2SO_4 with CeH_3 when applied to the observation for titanium hydride with

15 $\underline{M}$ DCl shows that the stoichiometry of the reaction is close to the ideal

equation

$$TiH_2 + 3D^+ = Ti^{+3} + H_2 + 3/2 D_2.$$
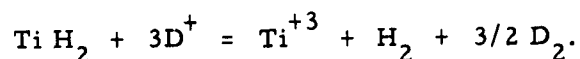
(D/H is only slightly in excess of the ideal value of 1.5.) With more dilute

HCl, the reaction is less rapid. Under these conditions, D/H is far in excess

of the ideal value of 1.5. Since D/H increases with succeeding samples, pro-

gressive exchange of the hydride with the solvent is indicated. The experi-

ments with strong oxidizing agents $TlCl_3$ and Ce(IV) suggest that a strongly

adhering coat of TiO_2 is formed. TiO_2 does not dissolve in the oxidizing mix-

tures, and in forming the oxide in the highest oxidation state, the oxidizing

agent seals itself off from the hydride.